

TRANSPORT OF SULFUR OXIDES WITHIN THE LOS ANGELES SEA BREEZE/LAND BREEZE CIRCULATION SYSTEM

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1. INTRODUCTION

The sea breeze/land breeze circulation system in the Los Angeles area results in transport of pollutants seaward at night followed by return of aged material inland the next day. This characteristic wind reversal pattern both increases the retention time available for the oxidation of SO_2 to form sulfates and causes individual air parcels to make multiple passes over large coastal emissions sources. As a result, the Los Angeles atmosphere exhibits high peak day and high annual mean sulfate concentrations in spite of the fact that sulfate concentrations in marine background or desert air are low.

The problem of identifying the impact of individual emissions sources on sulfate air quality in such a situation is so complicated that it will frustrate many conventional air quality modeling approaches. Transport and chemical reaction processes must be followed for several consecutive days within an airmass that "sloshes" back and forth over thousands of emissions sources. Unsteady meteorological conditions characterized by light and variable winds render Gaussian plume calculations inappropriate. The large spatial domain needed to confine several days' emissions, combined with the absence of meteorological data over the ocean make even finite difference scheme grid-based air quality models unattractive.

However, over the past five years a series of research projects have shown how SF_6 tracer studies combined with chemical modeling can be used to verify the origin of the high sulfate levels observed in Los Angeles. Transport patterns, dispersion rates and SO_2 oxidation rates have been measured during SF_6 tracer experiments. Emissions to air quality models have been constructed and validated using data from the tracer studies. Source contributions to observed sulfate air quality have been separated into the impact of distinctly different types of emissions sources. Emissions control strategies aimed at sulfate air quality improvement have been designed.

The purpose of this paper is to review and integrate the findings of research projects at Caltech which bear on the resolution of the Los Angeles sulfate air quality problem.

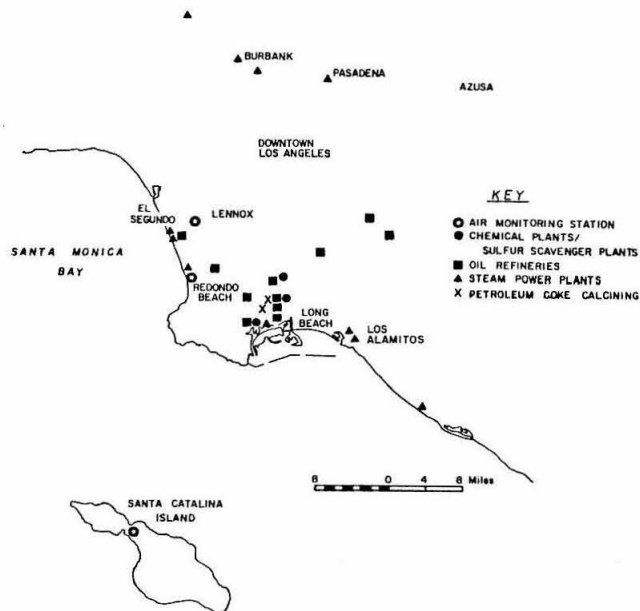


Figure 1. Major Sources of Sulfur Oxides Emissions in the Los Angeles Area.

The original reports on each individual project are cited and are available elsewhere.

2. SULFUR OXIDES EMISSIONS

The location of interest is the Southern California coastline of metropolitan Los Angeles and Orange Counties, as shown in Figure 1. The major sources of sulfur oxides emissions are located along the coast, close to waterborne transportation and a supply of cooling water.

Emissions from these sources during each month of the years 1972 through 1974 are shown in time series in Figure 2. An underlying contribution to sulfur oxides emissions from mobile sources is shown which exhibits only slight seasonal variation. To that is added a contribution from miscellaneous stationary sources, primarily from petroleum coke calcining kilns. The petroleum refinery emissions shown arise principally from refinery fluid catalytic cracking units. The

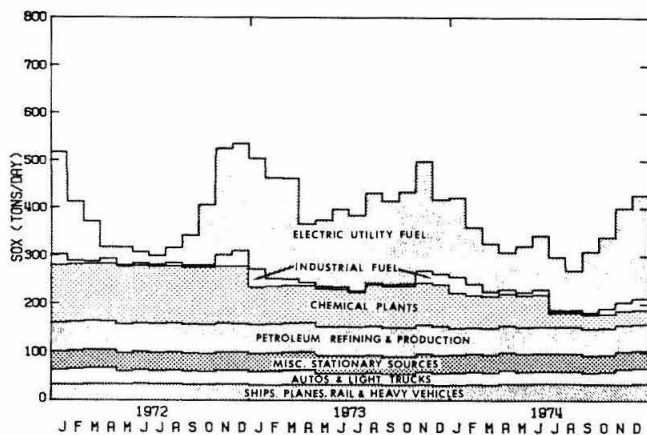


Figure 2. Sulfur Oxides Emissions within the Geographic Area Shown in Figure 1. (from Cass, 1978)

chemical plant emissions arise from sulfur recovery and sulfuric acid plants which reclaim by-products from refinery wastes. A strong seasonal variation in power plant and industrial fuel burning SO_x emissions is evident as interruptible natural gas customers switch to fuel oil in the winter months in order to free natural gas supplies for home heating use. Of particular interest to this study are the two groups of large power plants located at El Segundo and at Los Alamitos (see Fig. 1) which will be the subject of SF_6 tracer releases.

3.

LOS ANGELES SULFATE AIR QUALITY

Historical routine air monitoring data for sulfates and SO_2 were assembled and reviewed by Cass (1975; 1978). It was found that SO_2 concentrations in Los Angeles dropped rapidly with distance inland from major coastal point sources, as would be expected for dispersion of a conserved or slowly decaying pollutant species. In contrast, sulfate concentrations throughout the entire Los Angeles Basin averaged between 10 and $14 \mu\text{g}/\text{m}^3$ over long periods of time, and were as high in the immediate vicinity of major sulfur oxides sources as in the far inland valleys (see Figure 3). Long distance transport of pollutants from other airsheds could not account for this behavior since air quality measurements at islands off the southern California coast and in desert areas surrounding Los Angeles all showed much lower sulfate concentrations, in the range 3 to $5 \mu\text{g}/\text{m}^3$, annual mean.

Two hypotheses were offered which might explain the observed spatial distribution of sulfate air quality (Cass, 1975). During periods of direct inland transport from source to receptors, the constant sulfate concentration with distance inland from the coast could be explained by a competition between dispersion which tends to lower pollutant concentrations and additional gas-to-particle conversion involving SO_2 which tends to build-up sulfate concentrations. An alternative possibility is that sulfate concentrations accumulate aloft near the coast during late night land breeze and early morning stagnation periods. This well-aged aerosol might then be swept across the basin the next day by the advancing

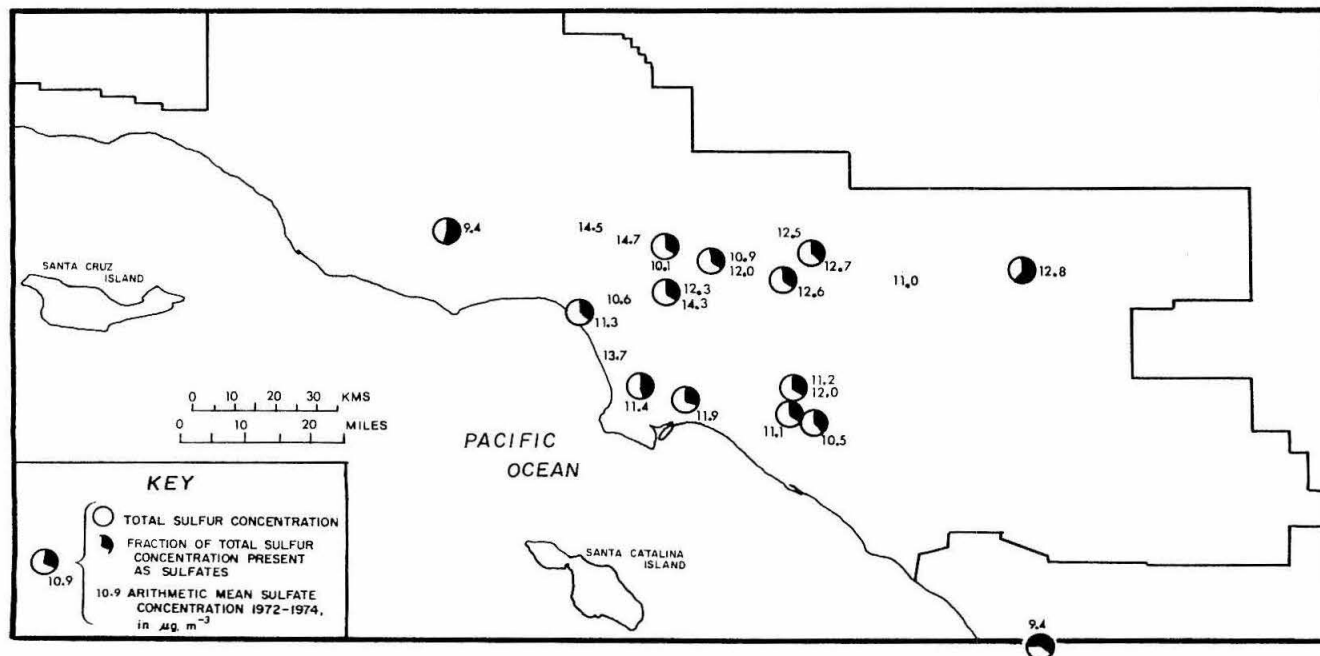


Figure 3. Arithmetic Mean Sulfate Air Quality: 1972 through 1974 Concentrations Shown Adjacent to Monitoring Site Location in $\mu\text{g}/\text{m}^3$ (from Cass, 1978).

5. SULFATE FORMATION IN THE SEA BREEZE/
LAND BREEZE CIRCULATION SYSTEM

Having verified the transport patterns and dispersion rates which occur under conditions when plumes are transported directly inland, attention was turned to the second flow regime of interest. Could it be shown that sulfur oxides air pollutants sent seaward at night by the land breeze were being returned inland the next day after having aged overnight in the marine environment?

A study of surface wind trajectories was conducted by Lyons (1975) to estimate the likelihood that pollutants sent seaward at night would return back across the Los Angeles County coast the next day. It was found, for example, that for a release at the surface into a land breeze at Redondo Beach in September or October 1973, there was an 89% probability that the tracer would be detected recrossing the coast within 19 hours after a 2:00 am release.

A series of field tests then were designed to confirm that pollutant recirculation also occurs for the case of elevated releases from large power plants (Shair et al. 1980). On July 22, 1977 SF₆ was released into the land breeze from a stack at the Southern California Edison Company El Segundo Generating Station. A total of 90 kg of SF₆ was discharged beginning at 00:00 hours Pacific Daylight Time on July 22 and ending at 05:00 hours on the morning of that day. SF₆ monitors were located aboard a ship traveling back and forth across Santa Monica Bay. The ship borne data showed that that power plant plume stayed aloft until about 5:30 am, after which fumigation to the ocean's surface occurred within a few minutes over a wide area of Santa Monica Bay.

Trajectories calculated from surface winds indicated that the emissions sent seaward tacked northward before recrossing the coastline the next morning. A line of closely spaced SF₆ monitors located at the coast however showed non-zero SF₆ concentrations returning inland from Ventura County south to Redondo Beach. Mass balance calculations performed on the SF₆ as it recrossed the line of coastal samplers showed that virtually 100% of the tracer could be accounted for, as shown in Figure 6. The peak returning SF₆ concentration recrossed the coast at the El Segundo monitoring site between 10:00 and 11:00 hours the next day. The point of highest pollutant impact thus crossed the coast the next morning near the point of pollutant origin. As it passed over the power plants and refinery complex at El Segundo for the second time, that air parcel would have received a second dose of pollutant emissions before beginning its journey across the Los Angeles Basin transported by the day's sea breeze.

A sulfate air quality monitoring station was established during this test at Lennox, which is located just inland from the El Segundo SF₆ release point. A second onshore sulfate monitoring station was set-up at Redondo Beach and a marine background site was established at Santa Catalina Island (Tsou et al., 1977). Data on SO₂ concentrations at Lennox and Redondo Beach are available from monitoring instruments operated by the South Coast Air Quality Management District.

Chemical reaction and ground level deposition calculations then were performed along the path of pollutant transport in order to determine the origin of pollutants contributing to the sulfate loading observed at Lennox (Cass and Shair, 1978). Urban backwash air parcels were defined as that material stored inland at the end of the prior day's sea breeze that was transported back to sea by the nighttime land breeze. These pollutants were tracked by means of surface wind trajectories.

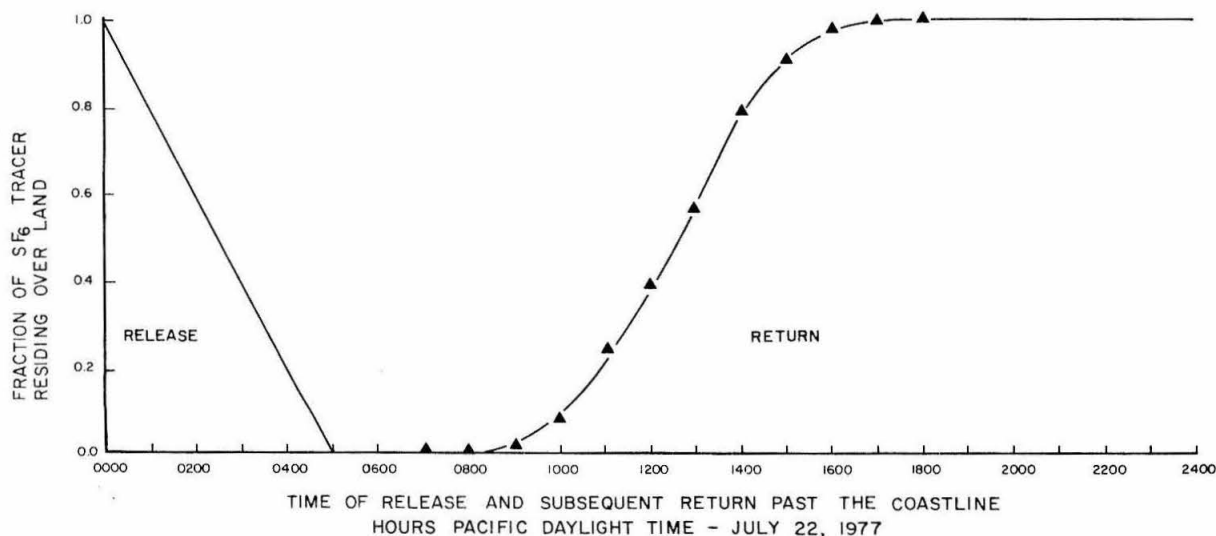


Figure 6. SF₆ Tracer Cumulative Release and Return From Emissions at El Segundo Power Plant into Nighttime Land Breeze Regime (from Cass and Shair, 1978).

Overnight emissions from the El Segundo area were identified by means of the SF_6 tracer. The intrusion of marine air uncontaminated by local emissions sources was identified by trajectory calculations and by reference to the Santa Catalina Island monitoring station. The presence at Lennox of fresh emissions released in the morning following the 5:00 am end of the tracer experiment were detected on the basis of sulfur balances on sulfate and total sulfur concentrations measured at Lennox. For the method of performing these air quality modeling calculations, see Cass and Shair (1978).

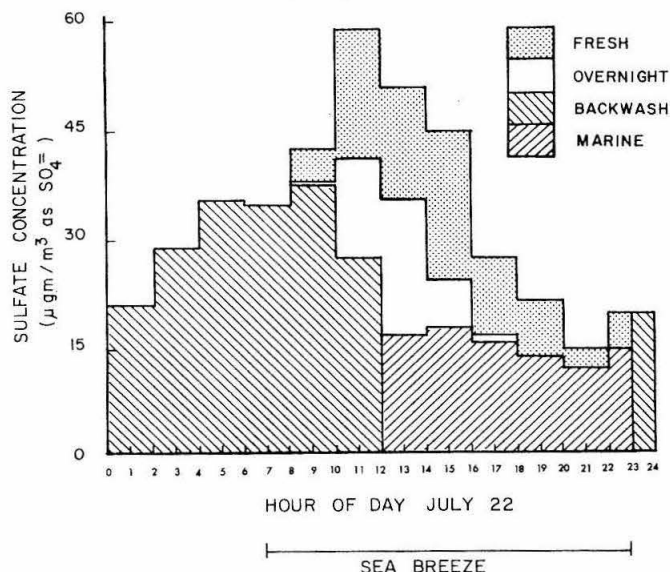


Figure 7. The Origin of Sulfate Concentrations Observed at Lennox July 22, 1977. (from Cass and Shair, 1978)

It was found that the total sulfur oxides concentrations observed that day at Lennox, California were dominated by freshly emitted SO_2 from nearby sources. In contrast, sulfate concentrations observed were due largely to the oldest material in the atmosphere. Measurements at Lennox on July 22 yielded a 24 hour average sulfate concentration of $32.3 \mu\text{gm}/\text{m}^3$ which as shown in Figure 7 consisted of:

- 49% sulfates held over from the previous day ("Backwash" recirculated by the land breeze/sea breeze reversal)
- 20% sulfates of marine background origin
- 20% sulfates from "fresh" emissions which occurred in the late morning and afternoon near the sampling site
- 11% sulfates from "overnight" emissions into the land breeze between midnight and the onset of the early morning sea breeze (tagged with SF_6).

The overall rate of SO_2 oxidation to form sulfates in the Los Angeles atmosphere was estimated to average about 5.8% per hour during these experiments.

6. SULFATE AIR QUALITY CONTROL STRATEGY DESIGN

An emissions control strategy study was conducted by Cass (1978) to assess the least costly means for reducing the ambient sulfate concentrations in the Los Angeles atmosphere. An important part of that study involved the construction and validation of a spatially and temporally resolved regional air quality model which relates sulfur oxides emissions to long-term average sulfate air quality. The SF_6 tracer studies played an important role in the model validation process by confirming parameter estimates for dispersion rates, SO_2 oxidation rates, and by providing a check on typical transport patterns.

The air quality simulation model developed computes pollutant concentrations from long-run average source to receptor transport and reaction probabilities. These transport and reaction probabilities in turn were estimated from Lagrangian marked particle statistics based on the time sequence of historical measured wind speed, wind direction, and inversion base height motion within the airshed of interest. First order chemical reactions and pollutant dry deposition were incorporated. The model was adapted to a multiple source urban setting in a way which permits retention of the air quality impact of each source class contributing to air quality predictions at each receptor site.

The calculation procedure used in that air quality model has been summarized briefly as follows. Single particles marked with the magnitude and initial chemical composition of sulfur oxides emissions from each source are inserted at measured time intervals into the atmosphere above the location of their points of origin. Depending on the plume rise characteristics of each source and meteorological conditions at the time of release, a pollutant parcel may be inserted either above or below the base of the temperature inversion which separates a well mixed layer next to the ground from a stable air mass aloft.

As these sulfur oxides laden air parcels are transported downwind, chemical reactions and surface removal processes act to alter the mass of SO_2 and sulfates represented by each particle. Sulfur oxides residing within the mixed layer next to the ground are affected both by ground level dry deposition and by atmospheric oxidation of SO_2 to form additional sulfates. Pollutant parcels stored within the stable layer aloft are isolated from surface removal processes but still are available for chemical reaction. Exchange of air parcels between the mixed layer next to the ground and the stable layer aloft occurs as inversion basing height changes over time.

The trajectories of successive particles released from a source form streaklines downwind from that source. Streaklines present at each hour of the month are computed and superimposed. The horizontal displacement of each particle located below the inversion base is paired with the particle's probable chemical status and divided by the depth of the mixed layer at the time that the streakline of interest was computed. The resulting magnitudes are assigned to a matrix of

receptor cells by summing the contribution for all particles falling within the same receptor cell. Totals are accumulated separately for SO_2 and for sulfates. The accumulated totals are divided by the dimensions of a receptor cell and the number of time steps being superimposed in order to directly obtain the spatial distribution of long-term average SO_2 and sulfate concentrations appearing throughout the airshed.

By repeating that process for each source in the airshed and superimposing the results onto an estimate of sulfate background air quality, a multiple source urban air quality model for sulfates is obtained. Superposition is permitted because all chemical processes are modeled in a form that is linear in emissions.

A grid system consisting of 2 mile by 2 mile squares was laid down over the geographic area shown in Figure 1. Emissions sources falling within each grid square were identified and separated into 26 classes of mobile and stationary sources within the 7 broad categories outlined in Figure 2. Each emissions source class was composed of a group of like equipment (e.g. sulfuric acid plants) that would be subject to compliance with a common emission control regulation.

The air quality model next was tested in Los Angeles over each month of the years 1972 through 1974. As shown in Figures 8 and 9, good agreement was obtained between computed and historically observed sulfate concentrations. Summertime SO_2 oxidation rates averaging 6% per hour were computed during the air quality modeling study, in

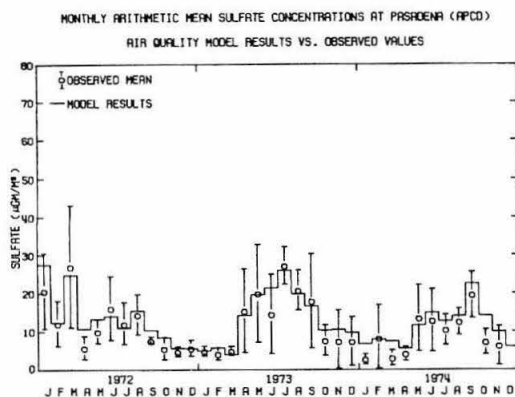


Figure 8. (from Cass, 1978)

good agreement with the results of the SF_6 tracer analysis described previously. A seasonal variation in SO_2 oxidation rate was inferred from air quality model calculations, with wintertime SO_2 oxidation rates declining to between 0.5% and 3.0% per hour. Transport paths downwind of the Los Alamitos power plants computed during periods of direct inland transport are shown in Figure 10 and may be compared to the SF_6 tracer study results of Figure 4.

All source class contributions to sulfate air quality computed from the air quality model are superimposed and averaged over the year 1974 in Figure 11. It is seen that the sulfate concentrations predicted in near coastal locations

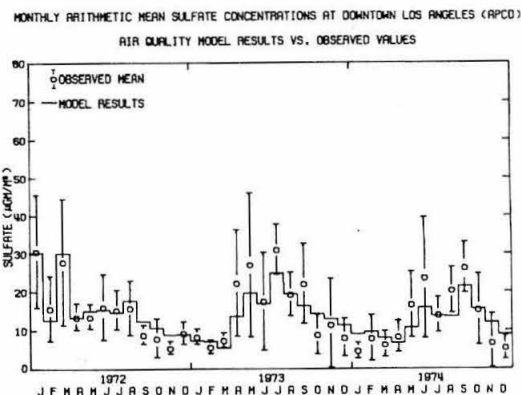


Figure 9. (from Cass, 1978)

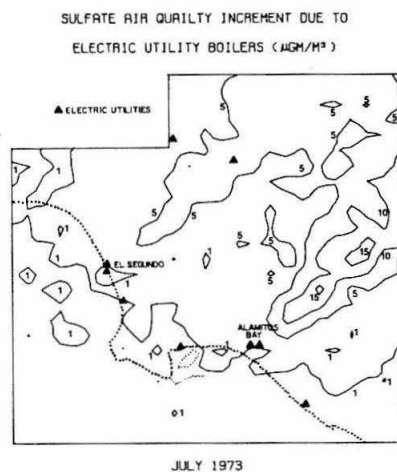


Figure 10. (from Cass, 1978)

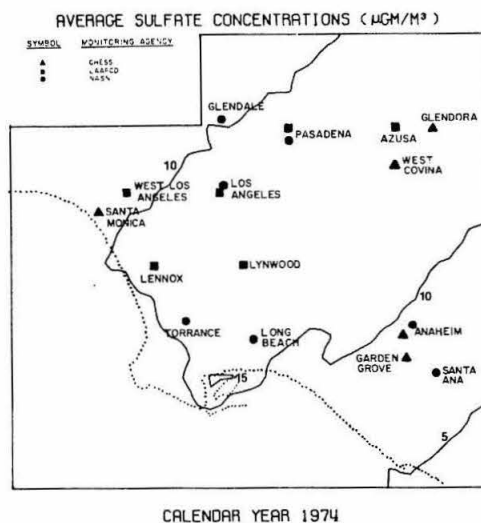


Figure 11. (from Cass, 1978)

are of the same magnitude as those computed far downwind, as must be the case if the air quality data of Figure 3 are to be closely reproduced.

In winter months with a pronounced daily sea breeze/land breeze wind reversal, air parcel trajectories wander widely over the basin. Sulfur oxides emitted from all source classes are dispersed widely within the airshed by the rotation of the wind vectors. In contrast, during mid-summer, onshore flow persists for most of the day. However, the sequential siting of major SO_x sources along the coast means that the central portion of the air basin is downwind of one major source group or another at most times. Lateral dispersion of emissions is just about sufficient to balance sulfate formation, with the result that upwind/downwind pollutant gradients are rather small in spite of the direct inland transport from sources to receptors. Annual mean sulfate concentrations are further smoothed by seasonal transport cycles in which peak sulfate concentrations appeared far inland during the summer and near the coast during the winter.

Source class contributions to observed sulfate air quality are shown in Figures 12 and 13. Superposition of small pollutant increments from power plants, heavy duty mobile sources, chemical plants, refineries and other sources, plus background sulfates must be considered in order to come close to explaining observed pollutant concentrations. Since no single type of emissions source dominates local sulfate air quality, a

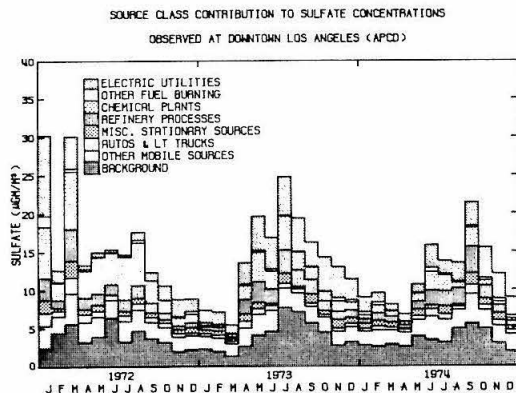


Figure 12. (from Cass, 1978)

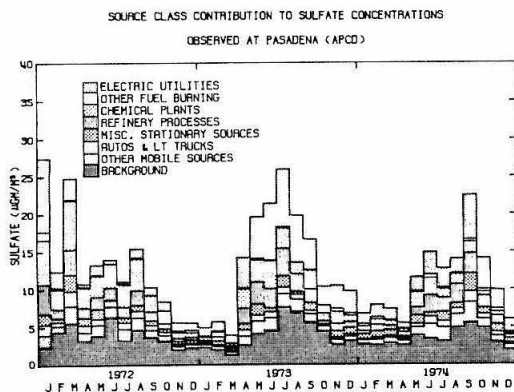


Figure 13. (from Cass, 1978)

control program diversified over a large number of emissions source types will be needed if a significant improvement in sulfate air quality is sought in the Los Angeles region. One such emission control strategy identified by Cass (1978) is shown in Figure 14, organized in order of increasing marginal cost per unit of sulfate concentration reduction.

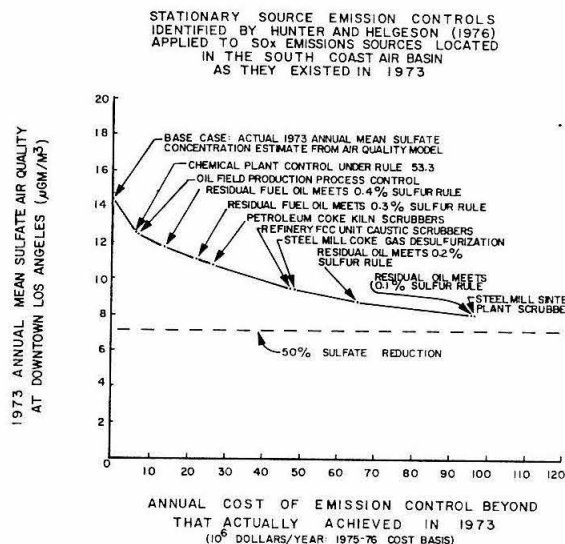


Figure 14. (from Cass, 1978)

7. CONCLUSIONS

The combination of SF_6 tracer studies and air quality modeling has been used to examine the transport and reaction of sulfur oxides air pollutants in the Los Angeles area atmosphere. The tracer studies provide an attractive means for obtaining data for air quality model validation studies involving very complex meteorological conditions.

The the course of these studies, several important hypotheses about the origin of the Los Angeles sulfate problem have been tested and confirmed. The sea breeze/land breeze circulation system in Los Angeles causes an increase in retention time for sulfate formation in this airshed. Pollutants held over from the previous day and pollutants emitted at night can be transported seaward on the land breeze, only to return many hours later as the sea breeze reversal in wind direction occurs. Both SF_6 tracer studies of single episodes and long-term air quality modeling studies indicate a summertime SO_2 oxidation rate which averages about 6% per hour.

Information gained from these studies holds important implications for emissions control strategies aimed at sulfate air quality improvement. From Figure 7 it is seen that peak sulfate concentrations near the coast can be caused by multiple passes of the same air mass over coastal point sources. This recirculation is induced by the sea breeze/land breeze system. Intermittent control strategies aimed at reducing sulfate concentrations by switching fuel at major sources on the same day as an episode forecast will achieve only limited

results. This is because so much of the material contributing to that day's sulfate concentrations is either held over from the previous day and night, or is due to long distance transport of regional background through the marine environment. If large sulfate concentration reductions are sought, it will probably be necessary to place continuous controls on emissions sources in order to prevent the build-up of sulfates on days preceeding the worst episodes. Air quality control strategy studies described in this paper have shown how emissions to air quality models can be used to identify combinations of emissions controls on a wide variety of sources that could cut long-term average sulfate concentrations in Los Angeles by about 50%.

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